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(54) **Drilling fluids**

(57) The use of aqueous surfactant compositions as, or in drilling fluids, including spacer fluids, packing fluids, or completion fluids, wherein said compositions comprise

(i) up to 5% by weight of one or more polymeric compounds

(ii) optionally, dissolved electrolyte,

(iii) up to 10% by weight of surfactant, said surfactant being present as an aqueous structured surfactant, which is a solution containing surfactant micelles or interspersed with a spherulitic surfactant, in a quantity sufficient to inhibit disintegration of shale and to maintain the rock cuttings in suspension under normal drilling conditions, and

(vi) 0 to 10% by weight of a weighting agent,

all weights being based on total weight of the composition.

A method of improving the drilling properties of conventional unweighted water based drilling fluids comprising one or more polymeric compounds and optionally dissolved electrolyte is also provided. Also drilling fluid compositions are provided.

GB 2 304 754

DRILLING FLUIDS

The present invention relates to aqueous Structured Surfactant drilling fluids which comprise polymeric compounds, typically dissolved electrolyte and low levels of surfactant, the use of such drilling fluids, and the preparation thereof. The drilling fluids of the invention do not require conventional amounts of fluid loss agents e.g. weighting agents such as barite, or other suspended solids such as clays to prevent fluid loss into surrounding rocks during drilling, and provide good fluid loss control even in the absence of said agents. Thus, the present invention provides effective unweighted Structured Surfactant drilling fluids, and Structured Surfactant drilling fluids comprising low levels of said weighting agents.

The term "Drilling Fluid" is used herein to refer to fluids used in the drilling of bore holes in rock to lubricate and cool drill bits, and to transport rock cuttings away from the rock face. The term is also used herein to include "Spacer Fluids", which are used to clean the sides of bore holes prior to cementing. Drilling Fluids are used in the construction of deep wells and bore holes, and especially oil and gas wells. For convenience the term Drilling Fluid as used herein also embraces "Completion Muds", which are used in civil engineering and the construction industry to stabilise holes and excavations by preventing the breakdown of shales on exposure to water. The term Drilling Fluid is also used herein to include "Packing fluids" which are used in drilling operations to fill the space between concentric, downhole tubing used in the well casing.

"Electrolyte" is used herein to denote those ionic compounds which dissociate at least partially in aqueous solution to provide ions, and which at the concentrations present tend to lower the total solubility (including micellar concentration) of surfactants in such solutions by a "salting out" effect. References herein to the Electrolyte content or concentration refer to the total dissolved Electrolyte, but excludes any suspended solid.

"Micelle" refers to a particle, which is either spherical or rod shaped, formed by aggregation of the surfactant molecules and having a radius less than twice the mean length of the surfactant molecules. The molecules in a Micelle are typically arranged such that their hydrophilic

("head") groups lie on the surface of the Micelle and the lipophilic ("tail") groups are in the interior of the Micelle.

"Bilayer" includes a layer of surfactant approximately two molecules thick, which is formed from two adjacent parallel layers, each comprising surfactant molecules which are disposed such that the lipophilic portions of the molecules are located in the interior of the Bilayer and the hydrophilic portions are located on its outer surfaces. "Bilayer" is also used herein to include interdigitated layers, which are less than two molecules thick. An interdigitated layer may be regarded as a Bilayer in which the two layers have interpenetrated allowing at least some degree of overlap between the tail groups of the molecules of the two layers.

"Spherulite" means a spherical or spheroidal body having dimensions of from 0.1 to 50 microns. Spherulites may sometimes be distorted into prolate, oblate, pear or dumbbell shapes.

"Vesicle" means a Spherulite containing a liquid phase bounded by a Bilayer. "Multiple Vesicle" means a Vesicle which contains one or more smaller Vesicles. The Spherulites present in Structured Surfactant systems are typically concentric Multiple Vesicles.

"G" phase refers to a liquid crystal Lamellar Phase, of the type also known in the literature as "neat" phase or "lamellar" phase. The "G" phase for any given surfactant or surfactant mixture normally exists in a narrow range of concentrations. Pure "G" phases can normally be identified by examination of a sample under a polarising microscope, between crossed polarisers. Characteristic textures are observed in accordance with the classic paper by Rosevear, JAOCS Vol. 31 P628 (1954) or in J. Colloid and Interfacial Science, Vol. 20 No. 4, P.500 (1969). "G" phases normally exhibit a repeat spacing of from 50 to 70 nm, in X-ray diffraction or neutron scattering patterns. "Expanded G phase" means a "G" phase with a repeat spacing of 110 to 150 nm.

"Spherical G Phase" means Multiple Vesicles formed from substantially concentric shells of surfactant Bilayer alternating with aqueous phase with a "G" phase or Expanded G phase spacing. Typically conventional G phases may contain a minor proportion of Spherical G Phase.

"Lye" means an aqueous liquid phase containing Electrolyte, which phase separates from, or is interspersed with, a second liquid phase containing more Active Ingredient and less Electrolyte than the Lye phase.

"Spherulitic Composition" means a composition in which a major part of the surfactant is present as spherical G-phase, or which is principally stabilised against sedimentation by a Spherical G-phase.

"Structured Surfactant" as used herein means a fluid composition which has shear dependent viscosity and solid-suspending properties and which comprises a surfactant mesophase, which may optionally be dispersed in, or interspersed with an aqueous phase which is typically a Lye phase. The mesophase may, for example, comprise Spherulites, especially Spherical G-phase.

"Weighting Agent" means a water insoluble particulate mineral having a specific density greater than 3.5 and preferably greater than 4 e.g. barite or hematite which provides fluid loss control of the drilling fluid into the rock being drilled.

"Drilling Mud" is a Drilling Fluid which contains suspended mineral particles, such as rock cuttings and or Weighting Agents.

"Polymeric Compound" is used herein to refer to natural, modified or synthetic gums, or polymers, of salts thereof e.g. polyelectrolyte.

- 24 Drilling Fluids in oil wells are normally pumped continuously down the drill stem, through apertures in the drill bit and are then forced up to the surface through the annular space between the drill stem and the side of the hole, carrying the rock cuttings in suspension. At the surface the cuttings are separated from the Drilling Fluid and the latter is then recycled. Prior to cementing, the Drilling Fluid is replaced by a Spacer Fluid which transports loose particles from the hole and leaves a clean, water-wet surface to provide a good cement bond.
- 30 Completion Fluids are used to drill into the formation rock containing the oil/gas and must not block up the pores with solids. Therefore completion fluids are generally unweighted.

Certain rocks cause particular problems during drilling or excavation, due to their tendency to disintegrate in the Drilling Fluid to form "fines" which are very difficult to separate from the fluid and which rapidly build up in the recycle stream causing an increase in viscosity thereof. Chief among the problem rocks is shale which generally disintegrates in the presence of water.

Therefore, an acceptable Drilling Fluid needs to have a viscosity which is sufficiently low under conditions of shear to flow readily, but it must also possess solid suspending properties for the reasons given hereinabove. To achieve these conflicting requirements a thixotropic fluid is usually required. Moreover, it must not cause excessive breakdown of rocks such as shale due to the penetration of the fluid into the rock. If it is to be useful for deep drilling, the fluid must be thermally stable, and it is important that excessive loss of fluid into the formation should be avoided.

Hitherto, these requirements have almost always been achieved by using either an oil or an oil-in-water emulsion as the Drilling Fluid. The oil coats particles of shale and protects them from contact with water, thereby inhibiting their disintegration. However this in turn creates an environmental problem, especially in offshore drilling operations, when the rock cuttings are discarded. To avoid serious pollution the oil must be cleaned from the cuttings, before they can be dumped. It is difficult and expensive to reduce the oil contamination to currently permitted levels, but even these small amounts of residual oil are ecologically undesirable, and there is increasing pressure to replace oil based drilling fluids altogether.

These oil based Drilling Muds and Lubricants have contained minor proportions of surfactants as emulsifying agents for the oil or as dispersants for sludge. The surfactants have typically been present essentially as monolayers surrounding colloidal size droplets or particles of oil or dispersed solid. The protection of shale in Drilling Muds has been essentially due to the shale being coated with oil. The suspending properties and thixotropic character of oil based Drilling Mud has been provided by the interaction of the dispersed oil droplets.

The alternative of using conventional aqueous solutions which contain polymeric suspending agents or dispersants, polymeric thickening agents and/or bentonite to suspend the rock

cuttings is less environmentally harmful, and may be somewhat cheaper than the use of oil based muds, but only for shallow drilling, and where the formation presents no special problems. For deep drilling or for drilling, or digging, through problem formations such as shale, which is very frequently encountered in oil well drilling and excavation, these conventional cheap aqueous fluids are inadequate. They have insufficient thermal stability to withstand the high temperatures of deep formations and they cause breakdown of the shale due to the penetration of the water through the shale. Their lubricity is also generally inferior to that of oil based muds.

Attempts have been made to improve the performance of aqueous Drilling Fluids with a variety of special additives such as polymeric coating agents, and high concentrations of Electrolyte to help stabilise shale. These have substantially increased the cost of the fluid, but have not succeeded in providing an aqueous fluid with adequate performance to replace oil based muds for deep drilling. However, environmental pressure is increasingly compelling oil companies to adopt relatively expensive and technically inferior aqueous based fluids in place of the conventional oil based muds. Such aqueous based fluids need to be specially treated, eg. by the use of weighting agents such as barite or haematite in order to control water seepage into porous rocks such as shale, where the seepage causes the shale to expand, and ultimately produces the collapse of the drilled hole.

In the case of oil-free muds, the protection of the shale has been provided by the presence of polymers which encapsulate the rock particles irreversibly and are therefore consumed quantitatively when the rock is separated. The solid suspending properties are provided by polymeric thickeners such as sodium carboxymethyl cellulose or methacrylates. These tend to stabilise the suspension at the expense of the mobility of the fluid.

Electrolytes have been used in both oil based and water based Drilling Mud to control the water activity. If the concentration of the Electrolyte is sufficiently high to reduce the water activity of the mud to the same level as that of the shale, hydration of the latter will not occur. However, if the water activity of the mud is too low the shale will tend to dehydrate and become brittle and if it is too high it will tend to hydrate and disintegrate, unless there is some protective barrier between the shale and the aqueous medium. Unfortunately it is not possible consistently to maintain the Electrolyte at the optimum level because the mineral strata

contain soluble salts which tend to dissolve in the mud altering the Electrolyte content as it passes through the hole.

Our UK Patent GB 2, 238,560 discloses aqueous Structured Surfactant based drilling fluids, which provide good thermal stability, which may be used for deep drilling operations and which do not comprise oils, such as mineral oils which is a potential pollutant and fire hazard. Reference is also made therein to the use of Structured Surfactants in laundry detergents, similar cleaning preparations, and pesticide compositions e.g GB 2,153,380. Typically, the drilling fluid compositions of GB 2,238,560 comprise more than 6% by weight of surfactant and a weighting agent such as barite (See Examples 1 to 9). Although the latter is not claimed to be an essential component for troublesome rocks such as shale, it is typically added to reduce the loss of the fluid through the rock. Thus, the compositions of GB 2,238,560 are believed to be limited application for drilling purposes where control of the loss of the fluid through the rock is required, but where it is desirable to avoid the use of a weighting agent. Furthermore, GB 2,238,560 teaches that it is preferable to avoid the use of suspending agents such as carboxymethyl cellulose, and polymeric thickening agents such as gums, in Structured Surfactant drilling fluids.

There is therefore a need for an aqueous based drilling fluid which has good drilling properties through problem rocks such as shale, but which does not require the presence of conventional amounts of a weighting agent, and which preferably is able to perform efficiently without said weighting agent i.e. an unweighting drilling fluid. Such an unweighted drilling fluid could for example be of particular benefit in drilling through said rocks when a completion fluid is required, as these fluids should preferably not contain weighting agents so that the bore hole sides may be kept clean and free of said weighting agent.

Furthermore, there is a need to be able to improve the drilling properties of conventional aqueous based drilling fluids through the aforementioned rocks, as required during drilling operations whenever such rocks are encountered, without requiring the use of the aforementioned weighting agents.

We have now discovered that aqueous surfactant drilling fluids which comprise typically up to 5% by weight of polymeric compounds, optionally dissolved electrolyte and up to 10% by

weight of surfactant, all weights being based on the total weight of the composition, exhibit good lubricity for both rock and metal, even under extreme pressure conditions in the absence of extreme pressure additives. Surprisingly these drilling fluids do not require the presence of weighting agents to protect rocks against disintegration due to the seepage of water. Also these compositions exhibit the rheological characteristics required for a drilling fluid, and are able to suspend solid rock cuttings. The fluid is easily separated from rock cuttings and any residual surfactant can easily be washed from the cuttings with water. The clean cuttings present no ecological hazard and may be safely dumped. The aqueous surfactant is a Structured Surfactant such as those formed by the interaction of surfactant with dissolved Electrolyte, preferably a spherulitic system. Typically it comprises a surfactant/water mesophase interspersed with an aqueous or aqueous Electrolyte continuous phase. The Structured Surfactants can readily be formulated in a heat stable form for high temperature applications such as deep drilling.

We have also discovered that aqueous Structured Surfactants drilling fluids which comprise up to 5% by weight of polymeric compounds, optionally dissolved electrolyte and up to 10% by weight of surfactant and up to 10% by weight of a weighting agent, all weights being based on the total weight of the composition, exhibit good lubricity for rock and metal, even in the absence of extreme pressure additives, with the advantages as mentioned hereinabove.

In our invention both suspending properties and protection of shale are provided to some extent essentially by the surfactant, preferably in conjunction with some dissolved Electrolyte. While we do not wish to be limited thereby, we believe that the surfactant may coat shale particles reversibly. It may also help to maintain an optimum water activity. The surfactant is preferably present in our composition as spherical G-phase or Micelles.

We have further discovered that the drilling properties through shale, or similar rocks which are susceptible to disintegration, of conventional water based drilling fluids which contain polymeric compounds, optionally dissolved electrolyte, but which do not contain weighting agents, are dramatically improved by the addition of up to 10% by weight of surfactant, based on the total weight of the composition, to produce an aqueous Structured Surfactant composition. The addition of surfactant to the conventional water based drilling fluid may be

made as required during the drilling operation in response to the drilling rocks and conditions encountered, or may be made during preparation of the drilling fluid to provide a ready formulated drilling fluid.

5 According to a first embodiment the present invention provides the use of aqueous surfactant compositions as, or in Drilling Fluids, including spacer fluids, packing fluids, or completion fluids, wherein said compositions comprise up to 5% by weight of one or more polymeric compounds, optionally dissolved electrolyte, and up to 10% by weight of surfactant, said surfactant being present as an aqueous Structured Surfactant, and further wherein said
10 composition comprises 0 to 10% by weight of a weighting agent, or suspended clay all weights being based on total weight of the composition.

15 In particular the present invention provides a method of drilling bore holes, said method comprising using as a Drilling Fluid, an aqueous structured surfactant which is preferably a solution containing surfactant micelles or interspersed with a spherulitic surfactant, in a quantity sufficient to inhibit disintegration of shale and to maintain the rock cuttings in suspension under normal drilling conditions.

20 According to a second embodiment the present invention provides a method of improving the drilling properties through rocks which are susceptible to disintegration upon contact with water, of conventional unweighted water based drilling fluids which comprise one or more polymeric compounds and optionally dissolved electrolyte, by the addition to said drilling fluids of up to 10% by weight of total surfactant, based on the total weight said fluid.

25 According to a third embodiment the present invention provides a drilling fluid composition comprising :-

- (i) 0.05 to 10% by weight surfactant, and
- (ii) up to 5% by weight of one or more polymeric compounds, and
- (iii) optionally dissolved electrolyte, and
- 30 (iv) 0 to 5% by weight of an antifoam.
- (v) 0 to 10% by weight of a weighting agent or suspended clay.

all weights being based upon the total weight of the composition, wherein said surfactant is present as a Structured Surfactant which comprises (a) an aqueous phase and (b) a spherulitic surfactant structure interspersed with said aqueous phase, in an amount sufficient to confer solid suspending properties thereon.

The surfactant may consist of a single surfactant or may be a mixture of one or more surfactants. Typically the surfactant may comprise a nonionic and/or anionic surfactants. Non-ionic surfactants are preferred although anionic, cationic and/or amphoteric surfactants may also be present therewith. In compositions comprising a non-ionic surfactant and another surfactant, it is preferred that at least an equal proportion of the surfactant is non-ionic surfactant.

Non-ionic surfactants which may be used according to the invention include in particular, alkyl or alkenyl alkoxylates, such as fatty alcohol alkoxylates and fatty acid alkoxylates, especially fatty alcohol ethoxylates and fatty acid ethoxylates. Particularly preferred non-ionic surfactants include, for example, lauryl alcohol ethoxylates, and oleic acid ethoxylates i.e. polyethylene glycol monooleate.

Said alkyl or alkenyl groups are preferably C_1 to C_{24} straight chain primary groups but may optionally be secondary, or branched chain groups, preferably C_4 to C_{20} groups, most preferably C_6 to C_{11} groups. Said alkoxylates preferably contain up to 50 alkoxylate groups, most preferably up to 20 alkoxylate groups, e.g. up to 10 alkoxylate groups. The alkoxylates include the ethoxylated, propoxylated, butoxylated and mixed alkoxylates thereof.

Other suitable non-ionic surfactants include for example a C_{10} - C_{12} alkanolamide of a mono or di-lower alkanolamine, such as coconut or tallow monoethanolamide or diethanolamide.

Other non ionic surfactants which may be present include ethoxylated alcohols, ethoxylated amines, ethoxylated alkylolamides, ethoxylated alkylphenols, ethoxylated glyceryl esters, ethoxylated sorbitan esters, ethoxylated phosphate esters, and the propoxylated, butoxylated and mixed ethoxy/propoxy and/or butoxy analogues of all the aforesaid ethoxylated nonionics, all having a C_{8-22} alkyl or alkenyl group and up to 20 ethyleneoxy and/or propyleneoxy and/or butyleneoxy groups, or any other nonionic surfactant which has hitherto been incorporated in

powder or liquid detergent compositions e.g. amine oxides. The latter typically have at least one C_{1-22} , preferably C_{10-20} alkyl or alkenyl group and up to two lower (e.g. C_{1-4} , preferably C_{1-2}) alkyl groups.

The preferred nonionics for our invention are for example those having an HLB range of 2-18 e.g. 8-18.

The surfactant may include an anionic surfactant as either the major proportion of the total surfactant or as a minor proportion thereof. It is preferred that the anionic surfactant is present in an equal or a minor proportion of the total surfactant when a non ionic surfactant is present. Very surprisingly, in certain circumstances it may be advantageous to use low concentrations of anionic surfactant in combination with an anionic surfactant. The anionic surfactant may for example be an at least sparingly water-soluble salt of sulphonic or mono esterified sulphuric acids e.g. an alkylbenzene sulphonate, alkyl sulphate, alkyl ether sulphate, olefin sulphonate, alkane sulphonate, alkylphenol sulphate, alkylphenol ether sulphate, alkylethanolamide sulphate, alkylethanolamide ether sulphate, or alpha sulfo fatty acid or its esters each having at least one alkyl or alkenyl group with from 8 to 22, more usually 10 to 20, aliphatic carbon atoms. Said alkyl or alkenyl groups are preferably straight chain primary groups but may optionally be secondary, or branched chain groups. The expression "ether" hereinbefore refers to oxyalkylene and homo- and mixed glyceryl-oxyethylene, glyceryl-oxypropylene groups, or glyceryl-oxyethylene-oxypropylene groups, typically containing from 1 to 20 oxyalkylene groups. For example, the sulphonated or sulphated surfactant may be sodium dodecyl benzene sulphonate, potassium hexadecyl benzene sulphonate, sodium dodecyl dimethyl benzene sulphonate, sodium lauryl sulphate, sodium tallow sulphate, potassium oleyl sulphate, ammonium lauryl monoethoxy sulphate, or monethanolamine cetyl 10 mole ethoxylate sulphate.

It is preferred that said anionic surfactant is an isopropylamine or lower alkyolamine, e.g. a mono, di or triethanolamine, salt of a $C_{10} - C_{14}$ benzene sulphonic acid, e.g. a monoethanolamine salt of benzene sulphonic. With such surfactants in the absence of any non-ionic surfactant it is preferred that they form the whole or predominant part of the total surfactant.

Other anionic surfactants which may be used include fatty alkyl sulphosuccinates, fatty alkyl ether sulphosuccinates, fatty alkyl sulphosuccinamates, fatty alkyl ether sulphosuccinamates, acyl sarcosinates, acyl taurides, isethionates, soaps such as stearates, palmitates, resinates, oleates, linoleates, rosins soaps and alkyl ether carboxylates and saponins. Anionic phosphate esters including naturally occurring surfactants such as lecithin may also be used. In each case the anionic surfactant typically contains at least one aliphatic hydrocarbon chain having from 8 to 22 preferably 10 to 20 usually an average of 12 to 18 carbon atoms, an ionisable acidic group such as a sulfo-, acid sulphate, carboxy, phosphono- or acid phosphate group, and, in the case of ethers, one or more glyceryl and/or from 1 to 20 ethyleneoxy and/or propyleneoxy groups.

The anionic surfactants may be present as the sodium salts. Other salts of commercial interest include those of potassium, lithium, calcium, magnesium, ammonium, monoethanolamine, diethanolamine, triethanolamine and alkyl amines containing up to seven aliphatic carbon atoms, such as isopropylamine.

The compositions of the invention may contain cationic surfactants, which include quaternary amines having at least one long chain (e.g. C_{12-22} typically C_{16-20}) alkyl or alkenyl group optionally one benzyl group and the remainder of the four substituents short chain (e.g. C_{1-4}) alkyl groups. They also include imidazolines and quaternised imidazolines having at least one long chain alkyl or alkenyl group, and amido amines and quaternised amido amines having at least one long chain alkyl or alkenyl group. The quaternised surfactants are all usually salts of anions which impart a measure of water solubility such as formate, acetate, lactate, tartrate, chloride, methosulphate, ethosulphate, sulphate or nitrate.

Compositions of our invention may also contain one or more amphoteric surfactant, which include betaines, sulphobetaines and phosphobetaines formed by reacting a suitable tertiary nitrogen compound having a long chain alkyl or alkenyl group with the appropriate reagent, such as chloroacetic acid or propane sultone. Examples of suitable tertiary nitrogen containing compounds include: tertiary amines having one or two long chain alkyl or alkenyl groups and optionally a benzyl group; any other substituent being a short chain alkyl group; imidazolines having one or two long chain alkyl or alkenyl groups and amidoamines having one or two long

chain alkyl or alkenyl groups. Generally amphoteric surfactants are less preferred than non-ionic, or anionic, surfactants.

The specific surfactant types described above are only exemplary of the commoner surfactants suitable for use according to the invention. Any surfactant may be included. A fuller description of the principal types of surfactant which are commercially available is given in "Surface Active Agents and Detergents" by Schwartz Perry and Berch.

Generally we prefer that surfactants for use according to our invention should be substantially non-toxic, especially to marine life, we also prefer that the surfactants should be substantially stable at temperatures above 100°C, preferably above 120°C, especially above 150°C and, e.g. for deep drilling applications, above 180°C.

The compositions of the invention typically contain between 0.05% and 10% by weight of total surfactant, preferably between 0.5% and 8%, most preferably between 1% and 7%. The exact amount of surfactant used will depend for example, upon the nature of the surfactant or surfactants present, the ratio of surfactants if more than one surfactant is present, the amount and type of electrolyte and polymeric compound present, and the required rheology characteristics of the drilling fluid dependent upon different drilling conditions encountered.

The polymeric compound may consist of a single polymeric compound or of one or more polymeric compounds. It is generally preferred that more than one polymeric compound is present.

The polymeric compound may be any natural, modified or synthetic polymer or gum or salt thereof e.g. polyelectrolyte, used in conventional water based drilling fluids. Typically, the polymeric compound is an anionic or amphoteric polymeric compound, e.g. an anionic polyelectrolyte or mixture thereof. However, the use of nonionic polymers e.g. ethylene oxide polymers is not excluded.

Suitable natural and modified polymeric compounds include amongst others, modified gums such as water soluble cellulose derivatives e.g. carboxymethyl cellulose, methylcellulose and

hydroxyethyl cellulose; water soluble starch derivatives such as carboxymethyl starch, and natural gums such as xanthan gum, guar gum and acacia gum. Suitable synthetic polymeric compounds include amongst others, polyacrylates, polymethacrylates and poly alkyl methacrylates, polymaleates, polyacrylamides, polyvinylacetates, ethylene oxide polymers, polyvinyl pyrrolidones and any copolymers thereof, although this list is not considered exhaustive. Other suitable co-polymers include di-isobutylene/ maleic anhydride copolymers.

Preferably the polymeric compound is a carboxymethyl cellulose, xanthan gum, polyacrylate, polymethacrylate, polymaleate or any combination thereof.

Typically the polyelectrolyte is an anionic polyelectrolyte e.g. alkaline metal salt for example a sodium or potassium, salt or an alkaline earth metal salt for example a calcium salt. A particularly preferred anionic polyelectrolyte is for example sodium carboxymethyl cellulose.

The average molecular weight for the polymeric compound is typically within the range 100 to 1,000,000, preferably 500 to 500,000, most preferably 1000 to 50,000.

The polymeric compound is typically present in an amount of up to 5% by weight, based on the total weight of the composition, preferably up to 4%, most preferably up to 3% by weight. In some circumstances, the amount of polymeric compound may be greater than 5% by weight, dependent upon the particular polymeric compounds, surfactants and electrolytes employed. However for reasons of rheology and cost it is preferred that the polymeric compounds are present in an amount of up to 5% by weight.

Dissolved Electrolyte compounds are strongly preferred constituents of our compositions.

Although it is possible to prepare Structured Surfactants in the absence of Electrolyte, if the surfactant concentration is sufficiently high, the mobility of such systems is often insufficient unless the surfactant has been selected with great care. Addition of Electrolyte permits the preparation of mobile Structured Surfactants containing relatively low concentrations of surfactant.

Suitable Electrolytes include the water soluble alkali metal, ammonium and alkaline earth metal salts of the strong mineral acids. Particularly preferred are sodium and potassium salts especially the chlorides. However lithium, calcium and magnesium salts may also be present. Among salts that are useful may be included phosphates, nitrates, bromides, fluorides, condensed phosphates, phosphonates, acetates, formates and citrates. It is often particularly convenient, in the case of Drilling Fluids to make up the composition by diluting a concentrate on site with locally occurring natural brine (e.g. sea water in the case of offshore operations). This may be used to provide all or part of the Electrolyte content of the Drilling Fluid.

The Electrolyte may be present in concentrations up to saturation. Typically the less the amount of surfactant present, the more Electrolyte will be required to form a structure capable of supporting solid materials. We generally prefer to use higher concentrations of Electrolyte and lower concentrations of surfactant, and to select the cheapest Electrolytes on economic grounds. Thus Electrolyte is normally present in a concentration of at least 0.1% by weight based on the total weight of the composition, more usually at least 0.5% e.g. more than 0.75% preferably more than 1%. Usually, dependent upon the solubility of the electrolyte the concentration is less than 30% more usually less than 10% e.g. less than 8% by weight. Typically the concentration is between 1% and 7% by weight.

The maximum Electrolyte concentration depends, among other things, on the type of structure, and the viscosity required as well as considerations of cost. We prefer to form Spherulitic compositions as described in our aforementioned UK Patent GB2,238,650, our UK Patent GB 2,153,380, in order to obtain a satisfactory balance between acceptable mobility of the compositions and loading of suspended solids such as shale.

In the case of Drilling Muds and Spacer Fluids, it is usually desirable to supply to the hole a fluid that contains the necessary concentrations of surfactant and Electrolyte to form a solid suspending structure. However Electrolyte salts occurring in the rock through which the hole is being drilled may sometimes be capable of forming the structure in situ if only an aqueous surfactant is supplied. It is often preferred to supply an aqueous system containing less than the optimum amount of Electrolyte in order to allow for dissolution of Electrolyte minerals occurring in the hole.

The quantity of Electrolyte required, also depends on the nature and solubility of the surfactant. Generally surfactants with high cloud points need less Electrolyte than surfactants with low cloud point. With some surfactants, for example the isopropylamine salt of benzene sulphonic acid, no Electrolyte is required to form spherulities.

We prefer that the drilling fluids of our invention should have low foaming properties. While this can be achieved by selecting inherently low foaming surfactants, it is preferred to include antifoams such as silicone oil antifoams, phosphate esters, fatty alcohols or, less preferably, hydrocarbon oils.

When present the antifoam is typically used in concentrations of 0.01 to 5% by weight, preferably 0.1 to 3% by weight dependent upon the surfactants employed.

The drilling fluids of the present invention preferably do not contain weighting agents, and are thus unweighted drilling fluids. However, lower than conventional amounts of weighting agents may also be included, e.g. up to 10% by weight based on the total weight of the composition, preferably up to 5% by weight. Suitable weighting agents include amongst others haematite and barite.

Alternatively the drilling fluids of the present invention may comprise suspended clays in replacement of the whole or part of the weighting agent.

The drilling fluids of the present invention may optionally contain minor amounts of other functional components, for example solid lubricants such as graphite suspended in the aqueous structured surfactant, and auxiliary structuring agents such as bentonite although such additions are normally unnecessary to prevent fluid loss or to provide suspending properties and may be detrimental to rheological properties. It is preferred said auxiliary structuring agents are not present. If present, bentonite should preferably not be in excess of 5% by weight of the total composition. However the compositions of our invention are generally capable of tolerating the presence of bentonite adventitiously derived from minerals in the bore hole.

The compositions may also optionally contain a biocide such as glutaraldehyde, or preferably a tetrakis hydroxymethyl phosphonium salt such as THP sulphate or a mixture thereof with glutaraldehyde, to inhibit the growth of sulphate reducing bacteria which may cause corrosion of the pipes, spoilage of the fluid and/or infection of the formation.

The Drilling Fluids may under certain circumstances contain E.P. additives and corrosion inhibitors such as phosphite esters, phosphonates, polyphosphonates, chromates and zinc salts and the like. The corrosion inhibitor is preferably an organic chelating agent or other inhibitor of corrosion of metal surfaces by aqueous solutions.

We prefer that the Drilling Fluids of our invention are substantially free from oil or organic solvents, either water-miscible solvents such as lower mono or polyhydroxy alcohols, ketones and polyethers or water-immiscible solvents such aromatic hydrocarbons, and also from any hydrotropes such as urea, benzene sulphonate or lower alkyl benzene sulphonates. Solvents and hydrotropes tend to interfere with surfactant structuring and require the use of substantially increased amounts of surfactant and/or Electrolyte. They also increase the cost of the formulation without generally increasing performance. Oil and solvents are in addition highly undesirable on environmental grounds. We therefore prefer, if present at all, that oils, solvents and hydrotropes are each present in proportions less than 10%, more preferably less than 5%, most preferably less than 1%, e.g. less than 0.5%, usually less than 0.1% and most commonly less than 0.05% by weight, based on the weight of the composition.

In use the drilling fluids of the invention typically contain suspended solid which may comprise rock cuttings such as shale.

Preferably the compositions of the invention have a plastic viscosity as measured on a Fann viscometer of from 5 to 35 cps- that is 0.005 to 0.035 Pa sec preferably from 0.015 to 0.03 e.g. 0.02 to 0.025 Pa sec. We prefer that the composition should have a Yield Point greater than 15 lb/100ft² preferably from 30 to 50 especially from 35 to 45 e.g. 40 lb/100ft². These Yield points are approximately equal, respectively, to 7.25. Pa; 14 to 25 Pa; 17 to 22 Pa; and 20 Pa. We particularly prefer that the composition should have a ratio of Yield Point to Plastic Viscosity of from 1 to 2.5 especially 1.5 to 2 e.g. 1.8 expressed in cps and lb/100ft²

respectively. These ratios correspond approximately to : 50 to 120; 70 to 95; 85 expressed in SI units.

The compositions may be supplied as pre-formulated compositions by blending the components of the compositions to produce the drilling fluid. Any suitable order of mixing may be used, for example the electrolyte may be dissolved in the water, then the polymeric compound added followed by the surfactant, with the composition being mixed until homogenous.

Preferably, the compositions are prepared by the addition of the surfactant to a pre-formulated conventional aqueous drilling fluid which comprises polymeric compounds and optionally electrolyte, to produce a Structured Surfactant composition as required. This may occur for example if shale is encountered during a drilling operation requiring the drilling fluid to exhibit good fluid loss, properties but where it is preferable to avoid the addition of weighting agents.

Alternatively, the conventional aqueous drilling fluids may be supplied as concentrates and diluted prior to use with an electrolyte solution, e.g. brine and the required amount of surfactant.

The invention will further be illustrated by reference to the following Examples.

EXAMPLES

EXAMPLE 1 - DRILLING FLUID COMPOSITIONS

Drilling Fluid compositions were prepared containing :-

	Example 1A % by weight	Example 1B % by weight
Potassium Chloride	4.48%	4.48%
Sodium Carboxymethyl cellulose	0.9%	0.9%
Xanthan Gum	0.36%	0.36%
Polyethylene glycol monoleate ^a 1	-	5.0%
fatty alcohol + 4EO ^a 2	5.0%	-
Water	balance	balance

The samples were opaque spherulitic compositions, which were capable of suspending solid particles.

EXAMPLE 2 - FLUID LOSS CONTROL PROPERTIES

The fluid loss control properties of Examples 1A and 1B were tested against the following conventional weighted and unweighted structured surfactant compositions as comparisons:-

Table 1 :- weighted and unweighted comparative structured surfactant drilling fluids

	Example No				
	% by weight				
	C	D	E	F	G
C ₁₂₋₁₆ linear alkyl benzene sulphonate *3	5.4	-	5.4	-	-
coconut diethanolamide *4	8.0	9.0	8.0	9.0	9.0
Isopropylamine alkyl benzene sulphonate *5	-	6.0	-	6.0	6.0
Sodium Chloride	4.0	-	4.0	4.0	-
Potassium Chloride	-	4.0	-	-	4.0
Silicon Antifoam	0.5	0.5	0.5	0.5	0.5
Barite	-	-	25.0	25.0	25.0
Water	←----- balance ----->				

Examples 1A, 1B and C to G were tested in a standard API pressure filter test rig, with the examples being forced through a Whatman No 45 filter paper at 20°C under a 50 psi pressure (pressurised with nitrogen). The amount of each test fluid which was forced through the filter paper in a testing time of 30 minutes was measured by volume. The results for each test sample is given below as millilitres (mls) which passed through the filter paper during the test time.

Table 2 :- Test Results

Example	Volume
1A	4.4 mls
1B	4.8 mls
C	> 125 mls in 1 minute of test time
D	> 125 mls in 1 minute of test time
E	7.1 mls
F	7.6 mls
G	7.5 mls

The compositions of the invention, Examples 1A and 1B are shown to exhibit excellent fluid loss control properties, being superior to that exhibited by 'weighted' structured surfactant compositions. Conventionally, the volume in the above test should be less than 5 mls in order to pass the fluid loss control test.

*1 available commercially as Empilan BQ100

*2 available commercially as Empilan KB4

*3 available commercially as Nansa 1169

*4 available commercially as Empilan CDE

*5 available commercially as Nansa YS94

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CLAIMS

1. The use of aqueous surfactant compositions as, or in Drilling Fluids, including spacer fluids, packing fluids, or completion fluids, wherein said compositions comprise
 - (i) up to 5% by weight of one or more polymeric compounds
 - (ii) optionally, dissolved electrolyte,
 - (iii) up to 10% by weight of surfactant, said surfactant being present as an aqueous Structured Surfactant, which is a solution containing surfactant micelles or interspersed with a spherulitic surfactant, in a quantity sufficient to inhibit disintegration of shale and to maintain the rock cuttings in suspension under normal drilling conditions, and
 - (vi) 0 to 10% by weight of a weighting agent,

all weights being based on total weight of the composition.
2. A method of improving the drilling properties of conventional unweighted water based drilling fluids, wherein said drilling fluid comprises
 - (i) one or more polymeric compounds, and
 - (ii) optionally, dissolved electrolyte,

wherein said method comprises the addition to said drilling fluids of up to 10% by weight of total surfactant, based on the total weight said fluid.
3. A drilling fluid composition comprising :-
 - (i) 0.05 to 10% by weight surfactant,
 - (ii) up to 5% by weight of one or more polymeric compounds,
 - (iii) optionally, dissolved electrolyte,
 - (iv) 0 to 5% by weight of an antifoam,
 - (v) 0 to 10% by weight of a weighting agent,

all weights being based upon the total weight of the composition,

wherein said surfactant is present as a Structured Surfactant which comprises (a) an aqueous phase and (b) a spherulitic surfactant structure interspersed with said aqueous phase, in an amount sufficient to confer solid suspending properties thereon.

4. A composition according to Claim 3 wherein said composition comprises 0.05 to 7% by weight surfactant.
 5. A composition according to Claim 3 or 4 wherein said surfactant is a non-ionic and/or anionic surfactant.
 6. A composition according to Claim 5 wherein said surfactant is an alkyl or alkenyl alkoxylate.
 7. A composition according to Claim 6 wherein said alkyl or alkenyl alkoxylate is a fatty alcohol ethoxylate or fatty acid ethoxylate.
 8. A composition according to Claim 7 wherein said fatty alcohol ethoxylate or fatty acid ethoxylate is a C_6 to C_{18} fatty alcohol or fatty acid ethoxylate with 1 to 10 ethoxylate groups.
 9. A composition according to Claim 5 wherein said anionic surfactant is a water soluble salt of an alkyl benzene sulphonic acid.
 10. A composition according to any one of Claims 3 to 9 wherein said composition comprises up to 3% by weight of one or more polymeric compounds.
-
11. A composition according to Claim 10 wherein said one or more polymeric compound is a natural, modified or synthetic polymer or gum, or salt thereof e.g. polyelectrolytes.
 12. A composition according to Claim 11 wherein said gum is xanthan gum, guar gum, carboxymethyl cellulose, or acacia gum.

13. A composition according to Claim 11 where said polymer is a polyacrylate, polymethacrylate, or polymaleate.
 14. A composition according to Claim 11 wherein said polyelectrolyte is an anionic polyelectrolyte e.g. sodium carboxymethyl cellulose.
 15. A composition according to any one of Claims 3 to 14 wherein said composition comprises up to 10% by weight of dissolved electrolyte.
 16. A composition according to Claim 15 wherein said electrolyte comprises an alkali metal or alkaline earth metal salt.
 17. A composition according to Claim 16 wherein said salt is a halide.
 18. A composition according to any one of Claims 3 to 17 wherein said antifoam is present in an amount of up to 3% by weight.
 19. A composition according to Claim 18 wherein said antifoam is a silicon antifoam.
 20. A composition according to any one of Claims 3 to 19 wherein said weighting agent is present in an amount of up to 5% by weight.
 21. A composition according a Claim 20 wherein said weighting agent is barite or haematite.
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22. A composition according to any one of Claims 3 to 21 wherein said composition further comprises suspended clays.



Applicati n No: GB 9517371.2
Claims searched: 1 & 3-22

Examiner: D.B.Pepper
Date of search: 9 November 1995

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.N): E1F FGP.

Int CI (Ed.6): C09K.

Other: Online: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	GB 2279080 A (Albright & Wilson)	
A	GB 2238560 A (Albright & Wilson)	
A	GB 2084225 A (Union Carbide Corp)	

X	Document indicating lack of novelty or inventive step.	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.